On the low-temperature lattice thermal transport in nanowires

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Abstract

We propose a theory of low temperature thermal transport in nano-wires in the regime where a competition between phonon and flexural modes governs the relaxation processes. Starting with the standard kinetic equations for two different types of quasiparticles we derive a general expression for the coefficient of thermal conductivity. The underlying physics of thermal conductance is completely determined by the corresponding relaxation times, which can be calculated directly for any dispersion of quasiparticles depending on the size of a system. We show that if the considered relaxation mechanism is dominant, then at small wire diameters the temperature dependence of thermal conductivity experiences a crossover from $T^{1/2}$ to T^3-dependence. Quantitative analysis shows reasonable agreement with resent experimental results.

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Low-dimensional materials have attracted considerable attention in recent years, particularly, in view of their potential applications in electronic devices [1, 2]. Many theoretical and experimental studies of nanowires and nanotubes are centered on the properties of electronic transport. However it is realized now that the thermal properties of nanomaterials are also important for applications [3, 4, 5]. It is of special interest to increase thermal conductance in the micro and nanodevices [1, 6, 7]. In this paper study thermal transport in nonmetallic systems, in which heat is transported by thermal excitations only. In addition to practical importance of such studies, thermal transport in nanowires is interesting from fundamental point of view. Recent theoretical [8] and experimental [9] findings proved the existence of the quantum of thermal conductance in ballistic regime, which is similar to the quantum of electronic conductance. The state of experimental and theoretical understanding of thermal transport in nanoscale systems is comprehensively discussed in the review [10]. Recently D. Li et al [11] reported an accurate measurement of lattice thermal conductivity in silicon nanowires for a wide range of temperatures and wire diameters. They demonstrated the significant influence of the system size not only on the magnitude of the thermal conductivity coefficient, but also on its temperature dependence. It is well known that for large enough diameters of the wire and diffusive phonon - boundary scattering, thermal conductivity coefficient at low temperatures is proportional to T^3. But for small values of the wire diameters experiment [11] shows clear crossover from cubic to near linear dependence on the temperature. In the present paper we consider one particular relaxation mechanism which can explain the observed crossover.

Recently Mingo [12] carried out an accurate numerical study of thermal conductance of silicon nanowires to explain the decrease of the thermal conductivity coefficient with wire diameter observed in the experiment. He assumed that all the effects can be explained by the reconstruction of the phonon dispersion, where realistic phonon modes obtained from MD simulations were applied to general expression of the thermal conductivity coefficient. His numerical analysis shows excellent quantitative agreement with the experiment [11] for large enough diameters at high temperatures. As the system size becomes smaller, the approach fails to describe a sharp decrease of thermal conductance as well as qualitative change of its temperature dependence. This is likely because the Matheissen's rule has been used for evaluation of the phonon lifetime, which has rather restricted range of applicability (see e.g. [13] and references therein).

As it was noted in Ref. [14], decrease of the temperature increases the characteristic phonon wavelength and reduces the scattering probability at the boundary surface. This leads to a modification of the phonon spectrum. For ideal wires it is represented by a set of branches with energies proportional to 1D momentum directed along the wire. So the standard theory of thermal conductance in dielectrics and semiconductors has to be modified to account for low dimensionality effects as well as phonon spectrum modification at low temperatures. Thus, to understand thoroughly the physical processes occurring inside the nanowires with decreasing sizes, we need an analytical theory to account for different mechanisms explicitly, such as dispersion reconstruction and restricted geometry.

To approach the problem we consider low enough temperatures, where the quasiparticle states of "acoustic" branches are thermally populated ($\epsilon \longrightarrow 0$ when $p \longrightarrow 0$). The corresponding acoustic branches have the following dispersion relations [14, 15]:

$$\epsilon_1 = u_1 p_1, \qquad \epsilon_2 = u_2 a p_2^2, \tag{1}$$

where ϵ_i stands for the energy of a quasiparticle, p_i is the corresponding momentum, a is the wire diameter, u_1 and u_2 are the characteristic velocities. The first expression in Eq. (1) is the phonon dispersion and the second expression is the dispersion of flexural mode. The nature of flexural modes comes from the fact they are analogous to bending modes of classical elasticity theory, or the antisymmetric Lamb waves of a free plate [16]. Appearance of such a mode is just a direct consequence of restricted geometry, and under some conditions it can be considered as the only size effect in thermal transport properties. Strictly speaking there are two modes for each type of dispersion, but we do not account for them separately since their contributions are qualitatively the same. Consequently, we have to solve the kinetic problem for two-component gas of quasiparticles. It is well known [13, 17, 18, 19, 20] that using simple Callaway formula to estimate the thermal conductivity coefficient in two-component systems sometimes leads to serious confusions. Simple summation of the relaxation rates, as is done in the majority of theoretical works, is questionable under many physical conditions. The dependence of the kinetic coefficients on different relaxation times is much more complicated in reality. Accurate method for calculation of the diffusion coefficient in two-component gas of quasiparticles was proposed in Ref. [20]. Here we extend this formalism to thermal conductance problem.

To start, we consider a system of two types of quasiparticles. Their kinetics is described

by equations for corresponding distribution functions f_i:

$$v_i \frac{\partial f_i}{\partial z} = \sum_{j=1}^{2} C_{ij}(f_i, f_j) + C_{i3}(f_i), \qquad i = 1, 2. \tag{2}$$

where $C_{ij}(f_i, f_j)$ is the collision integral of thermal excitations, and $C_{i3}(f_i)$ is the collision integral describing the scattering processes between quasiparticles and scatterers. In general the latter includes all the processes leading to the non-conservation of the total energy. $v_i = \partial \epsilon_i / \partial p_i$ is the group velocity of the corresponding thermal excitation. The main purpose of our theory is to obtain analytic expressions of thermal conductance, which are applicable to quasiparticles with arbitrary dispersion relations. In other words, the explicit dispersion relations in Eq. (1) are needed only at the last stage when calculating corresponding relaxation times and thermodynamic quantities. As usual, we seek a perturbative solution of the system (2) in the form

$$f_i = f_i^{(0)} + \delta f_i, \tag{3}$$

where $f_i^{(0)}$ is the local equilibrium Bose-function and $\delta f_i \ll f_i^{(0)}$ represents small deviation from the equilibrium. The perturbation term can be conveniently chosen to be $\delta f_i = -g_i \partial f_i^{(0)} / \partial \epsilon_i$ with g_i the new target functions. After the standard linearization procedure, Eq. (2) can be written in the following matrix form:

$$|\phi_\kappa\rangle \frac{1}{T} \frac{\partial T}{\partial z} = \hat{C} |g\rangle, \tag{4}$$

where

$$|\phi_\kappa\rangle = \left| \begin{matrix} \epsilon_1 v_1 \\ \epsilon_2 v_2 \end{matrix} \right\rangle, \quad |g\rangle = \left| \begin{matrix} g_1 \\ g_2 \end{matrix} \right\rangle.$$

The 2D collision matrix $\hat{C}$ can be decomposed into a sum of three terms, corresponding to different relaxation mechanisms: $\hat{C} = \hat{J} + \hat{S} + \hat{U}$, where $\hat{J}$, with matrix elements $\mathcal{J}_{ij} = C_{ik}\delta_{ij} + C_{ij}(1-\delta_{ij})$ $(k \neq i)$, describes the relaxation due to interaction between quasiparticles of different types; $\hat{S}$ ($\mathcal{S}_{ij} = C_{ii}\delta_{ij}$) describes collisions between identical quasiparticles, and $\hat{U}$ ($\mathcal{U}_{ij} = C_{i3}\delta_{ij}$) describes all the other relaxation mechanisms, which do not conserve total energy of the quasiparticle system. $\hat{U}$ includes scattering on defects, boundaries, umklapp processes etc. [21] Here C_{ij} represent *linearized* collision operators.

Let us define the scalar product of two-dimensional bra- and ket-vectors as follows [20]:

$$\langle \phi | \chi \rangle = \sum_{k=1,2} (\phi_k | \chi_k) = -\sum_{k=1,2} \int \phi_k^* \chi_k \frac{\partial f_k^{(0)}}{\partial \epsilon_k} d\Gamma_k, \tag{5}$$

where $(\phi_k|$ and $|\chi_k)$ are the correspondent one-component vectors, $d\Gamma$ is the element of phase volume. Under this condition, the collision operator $\hat{\mathcal{C}}$ becomes hermitian. System (4) is the system of nonuniform linear integral equations. According to the general theory of integral equations the target solution $|g\rangle$ must be orthogonal to the solution of corresponding uniform equations $\hat{\mathcal{C}}|\phi_{uni}\rangle$. It is therefore convenient to write the formal solution of (4) so that the orthogonality condition $\langle g|\phi_{uni}\rangle$ is imposed explicitly in the solution. For this purpose we define the projection operator $\hat{\mathcal{P}}_n$ onto the subspace orthogonal to the vector $|\phi_{uni}\rangle$, $\hat{\mathcal{P}}_n = 1 - \hat{\mathcal{P}}_c$, $\quad \hat{\mathcal{P}}_c = |\phi_{uni}\rangle\langle\phi_{uni}|$. As a result, the formal solution of the system (4) can be written in the form

$$|g\rangle = \hat{\mathcal{P}}_n \left(\hat{\mathcal{C}}^{-1}\right) \hat{\mathcal{P}}_n |\phi_\kappa\rangle \frac{1}{T}\frac{\partial T}{\partial z}. \tag{6}$$

The heat flux density due to the thermal excitations of different types is given by the expression $Q = \sum_{k=1,2} \int \epsilon_k v_k f_k d\Gamma_k$. Using relation (3) and definition of scalar product (5), Q can be rewritten as $Q = \langle\phi_\kappa|g\rangle$. On the other hand, the effective thermal conductivity coefficient is defined by the relation $Q = -\kappa_{eff}\partial T/\partial z$. Comparing the above two expressions for Q, and using the formal solution (6) we obtain

$$\kappa_{eff} = -\frac{1}{T}\langle\phi_\kappa|\hat{\mathcal{C}}^{-1}|\phi_\kappa\rangle. \tag{7}$$

To derive an exact and analytical expression for thermal conductivity coefficient (7) it is necessary to introduce a complete set of orthonormal two-dimensional vectors $|\psi_n\rangle$ ($n = 1, 2, 3, ...$) belonging to the infinite-dimensional Hilbert space with scalar product (5). In principle, the particular choice of the basis is not essential, but for the convenience of calculations it is useful to specify at least four of them. It's convenient to chose the first of them to correspond to the total momentum of quasiparticles and the second one to be orthogonal, but still linear in momentum [20]:

$$|\psi_1\rangle = \frac{1}{\sqrt{\rho}}\left|\begin{matrix} p_1 \\ p_2 \end{matrix}\right\rangle, \quad |\psi_2\rangle = \frac{1}{\sqrt{\rho\rho_1\rho_2}}\left|\begin{matrix} \rho_2 p_1 \\ -\rho_1 p_2 \end{matrix}\right\rangle, \tag{8}$$

where $\rho_i = (p_i|p_i)$ is the normal density of the ith component, $\rho = \rho_1 + \rho_2$. The third and

the fourth vectors correspond to the energy flux:

$$|\psi_3\rangle = \frac{1}{\mathcal{N}_{\kappa 1}} \left| \begin{matrix} \psi_{\kappa 1} \\ 0 \end{matrix} \right\rangle, \quad |\psi_4\rangle = \frac{1}{\mathcal{N}_{\kappa 2}} \left| \begin{matrix} 0 \\ \psi_{\kappa 2} \end{matrix} \right\rangle, \tag{9}$$

where

$$\psi_{\kappa j} = \frac{1}{\sqrt{T}} \left(\epsilon_j v_j - \frac{S_j T}{\rho_j} p_j \right), \tag{10}$$

and $\mathcal{N}_{\kappa j} = \sqrt{(\psi_{\kappa j}|\psi_{\kappa j})}$ is the corresponding normalization coefficient. Partial entropy of quasiparticle subsystem S_j in eq. (10) is given by the relation

$$S_j = \frac{1}{T}(\epsilon_j v_j | p_j). \tag{11}$$

Formally, the kinetic problem of two-component quasiparticles system can be solved in the above basis set. The inversion of the operator matrix $\hat{\mathcal{C}}$ in Eq. (7) is similar to the procedure described in Ref. [20]. The final result contains infinite dimensional non-diagonal matrices. To obtain closed form expressions we must use some approximations, correct τ-approximation [19] or Kihara approximation [20, 22, 23]. In some physical situations we are able to obtain closed analytical expressions. It is rigorously proved in [20] that in case of quasi-equilibrium within each subsystem of quasiparticles, the corresponding transport coefficient can be obtained in close analytical form. This is a reliable approximation when the low temperature relaxation is mainly governed by the defect scattering processes. The approximation formally implies that all the matrix elements of matrix $\hat{\mathcal{S}}$ in eq. (7) tend to infinity. The thermal conductivity coefficient in this case can be obtained in the form: $\kappa_{eff} = \kappa_F + \kappa_D$. Here we separate the flux part of thermal conductivity coefficient $\kappa_F = \tau_F S^2 T / \rho$ with $S = S_1 + S_2$, which approaches infinity when the quasiparticles do not interact with scatterers, and the diffusive part $\kappa_D = \tau_D \left(S_1 T / \rho_1 - S_2 T / \rho_2 \right)^2 \rho_1 \rho_2 / T \rho$. The corresponding relaxation times are given by

$$\tau_D = \left\{ \frac{\rho_1}{\rho} \tau_{23}^{-1} + \frac{\rho_2}{\rho} \tau_{13}^{-1} + \tau_{12}^{-1} + \tau_{21}^{-1} \right\}^{-1}, \tag{12}$$

and

$$\tau_F = \tau_D \left(\frac{S_1}{S} \tau_{23}^{-1} + \frac{S_2}{S} \tau_{13}^{-1} + \tau_{12}^{-1} + \tau_{21}^{-1} \right)^2 (\tau_{13}^{-1} \tau_{23}^{-1} + \tau_{12}^{-1} \tau_{23}^{-1} + \tau_{21}^{-1} \tau_{13}^{-1})^{-1}. \tag{13}$$

6

Relaxation times contained in formulas (12) - (13) are defined by

$$\tau_{kj}^{-1} = \frac{1}{\rho_k}(p_j|C_{kj}|p_j).$$ (14)

We emphasize that they are not actual scattering times, which are momentum dependent, but are relaxation times associated with corresponding scattering mechanisms. Once we obtain the particular scattering rate $\nu_{kj}(p_k)$ from standard scattering theory, we can replace true collision operator C_k with $\nu_{kj}(p_k)$, so that the corresponding relaxation time can be calculated by

$$\tau_{kj}^{-1} = \rho_k^{-1} \int p_k^2 \nu_{kj}(p_k) \frac{\partial f_k^{(0)}}{\partial \epsilon_k} d\Gamma_k$$ (15)

As can be seen from the derived formulas, the coefficient of thermal conductivity contains different relaxation times in rather non-trivial combination. If drop out one component (say set $S_2 = 0$, $\rho_2 = 0$) we recover the usual result $\kappa_F^{(1)} = \tau_{13} S_1^2 T/\rho_1$. For phonons with linear dispersion $\epsilon = vp$, κ_F reduces to the well-known result $\kappa_F^{ph} = C_{ph} v^2 \tau_{13}/3$, where $C_{ph} = 3S_{ph}$ is the heat capacity of phonon gas.

The main advantage of our approach is its universality. In fact till now we have not restricted ourselves to any particular dimensionality of the system or any quasiparticles dispersion. All the necessary information is contained in the corresponding relaxation times and thermodynamic quantities. This formalism allows us to analyze contributions from different relaxation mechanisms to the total thermal conductivity coefficient. Given the dispersion relations of quasiparticles, we can easily calculate all the quantities contained in (12) - (13).

With Eqs. (12) - (13) we are able to address the competition between relaxation processes of the flexural and phonon modes. Glavin [14] noted that such a competition can be essential at extremely low temperatures if the dominant relaxation mechanism is elastic scattering on defects, where he argued that thermal conductivity coefficient would scale as $T^{1/2}$. Our approach allows us to study this competition comprehensively. Particularly, we predict the strong dependence of the temperature scaling exponent on the wire diameter. The standard Fermi golden rule approach [14] gives the momentum dependent scattering rates for different modes $\nu_{13} = W_{13}\frac{p^{1/2}}{u_1^3 a^{3/2}}$, $\nu_{23} = W_{23}\frac{1}{p u_2^3 a^3}$, where W_{kj} are the corresponding scattering amplitudes, which depend on the physical properties of particular material. Using Eq. (15) it is easy to show, that the corresponding relaxation times scale as

$$\tau_{13}^{-1} \propto a^{-3/2}T^{1/2}, \quad \tau_{23}^{-1} \propto a^{-5/2}T^{-1/2}.$$ (16)

Different temperature dependence of relaxation times lead to a strong competition between two physically different mechanisms of thermal conductivity, flux and diffusive. The dominance of one over the other strongly depends on the wire diameter at a given temperature. To make some specific conclusions let us summarize the approximations done and specify the range of validity of the proposed theory. We consider a situation when thermal excitations are multiply scattered elastically while being transferred through the wire, so that other scattering mechanisms are strongly suppressed by interaction with defects. Only for this case we were able to drop relaxation within each subsystem of identical quasiparticles to obtain closed expressions (12), (13). The influence of boundary is accounted in the dispersion of flexural mode and in the dimensionality of the system. The range of temperature is supposed to satisfy the relation $T < \Delta\epsilon$, where $\Delta\epsilon \sim 1/a$ is the characteristic value of the frequency gap between the adjacent phonon branches. For larger temperature we cannot use the acoustic modes (1) only, but need to account higher branches.

In Figure 1 we compare our theoretical results with the experimental data from [11]. We have chosen the unknown parameters $W_{13} = 1.2 \cdot 10^{-44} \mathrm{m}^5 \mathrm{s}^{-4}$ and $W_{23} = 0.9 \cdot 10^{-44} \mathrm{m}^5 \mathrm{s}^{-4}$ to fit data for $a = 22$nm. Deviations from the experimental data for large diameters and temperatures show the restriction of applicability of our initial approximations. They arise from the Debye approximation and simplified dispersion expression. Additionally, when the diameter of the wire increases, the mechanism we consider becomes less dominant. To be more precise we need to include higher excitation branches as well as another relaxation mechanisms. However our approach allows to understand the physics of the processes in the region under consideration. Clearly, observed crossover is the result of competition between $\kappa_F \propto T^{1/2}$ and $\kappa_D \propto T^3$. For smaller diameters, κ_F is strongly dominant in the wide range of temperatures as shown on Figure 2 for wire diameter $a = 2$nm. Figure 3 demonstrates a complete crossover from $T^{1/2}$ to T^3 dependence for the nanowire of $a = 30$nm. It can be seen that the T dependence between 20K and 40K is nearly linear, which was observed in the experiment [11]. It should be noted that T^3 dependence of κ_D cannot be interpreted in simple analogy with the bulk case. It comes not from a specific heat directly, but from different sources including competition of the relaxation times in Eqs. (12), (13).

In summary, we derived the general analytical expressions (12) - (13), to explicitly calculate the contributions of different scattering mechanisms to the total relaxation of the system. The simple expressions clarify the essential effects leading to the observed behavior

of thermal conductivity coefficient. It is clear that the particular dispersion laws (and their reconstruction) affect scattering rates and thermodynamic quantities. Restricted geometry and low dimensionality lead to additional scattering mechanisms. Note the information about dimensionality is naturally included in the particular form of phase space element $d\Gamma_i$. Such a formalism helps to distinguish effects from different scattering mechanisms. When applied to the regime, where phonon modes compete with flexural ones, our theory agrees favorably with available experimental data. Furthermore, we showed that the thermal conductivity coefficient changes from approximately $T^{1/2}$-dependence to T^3-dependence with increasing temperature. In view of our theoretical results it is useful to investigate smaller diameters or lower temperatures with fixed diameters in experiment to better reveal the crossover from T^3 to $T^{1/2}$ dependence.

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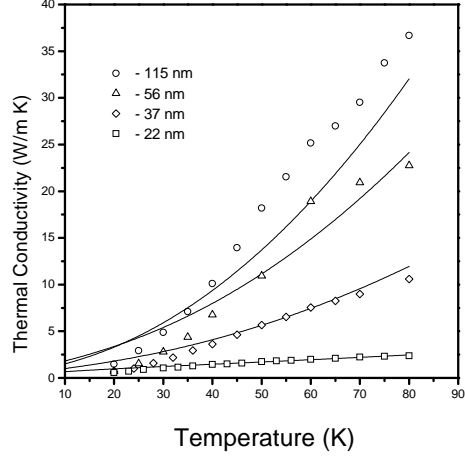[23] E. A. Mason, J. Chem. Phys. **27**, 782 (1957).

FIG. 1: Thermal conductivity coefficient calculated from Eqs. (12) and (13) for different values of nanowire diameter. Experimental data are from Ref. [11].
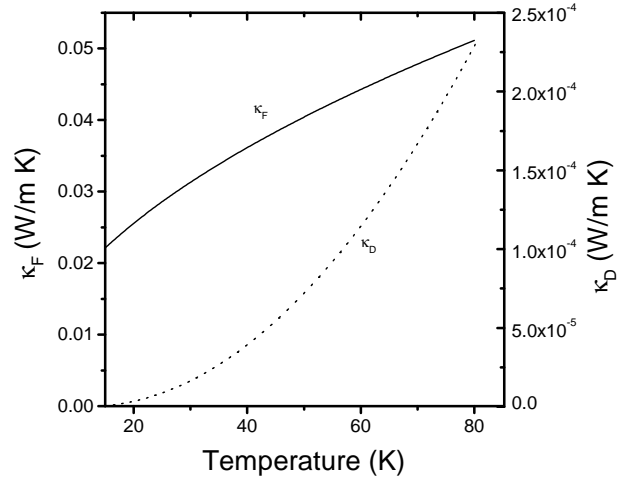

FIG. 2: Comparative contribution from flux and diffusive parts of thermal conductivity for a 2nm wire.
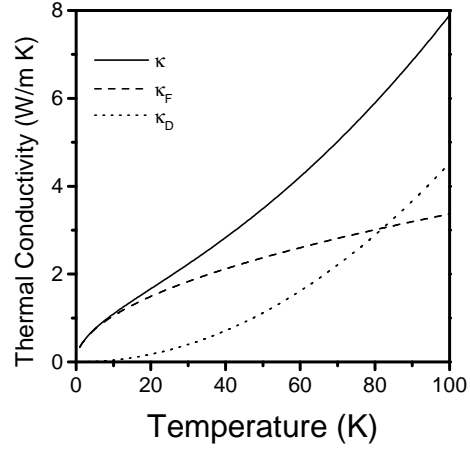
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FIG. 3: Crossover from $T^{1/2}$ to T^3 dependence of κ_{eff} for a 30nm wire.